

High-concentrated etherbased electrolytes for sulfidic semi-solid Li-S batteries with fully separated anolyte and catholyte

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Motivation

Liquid Li-S batteries:

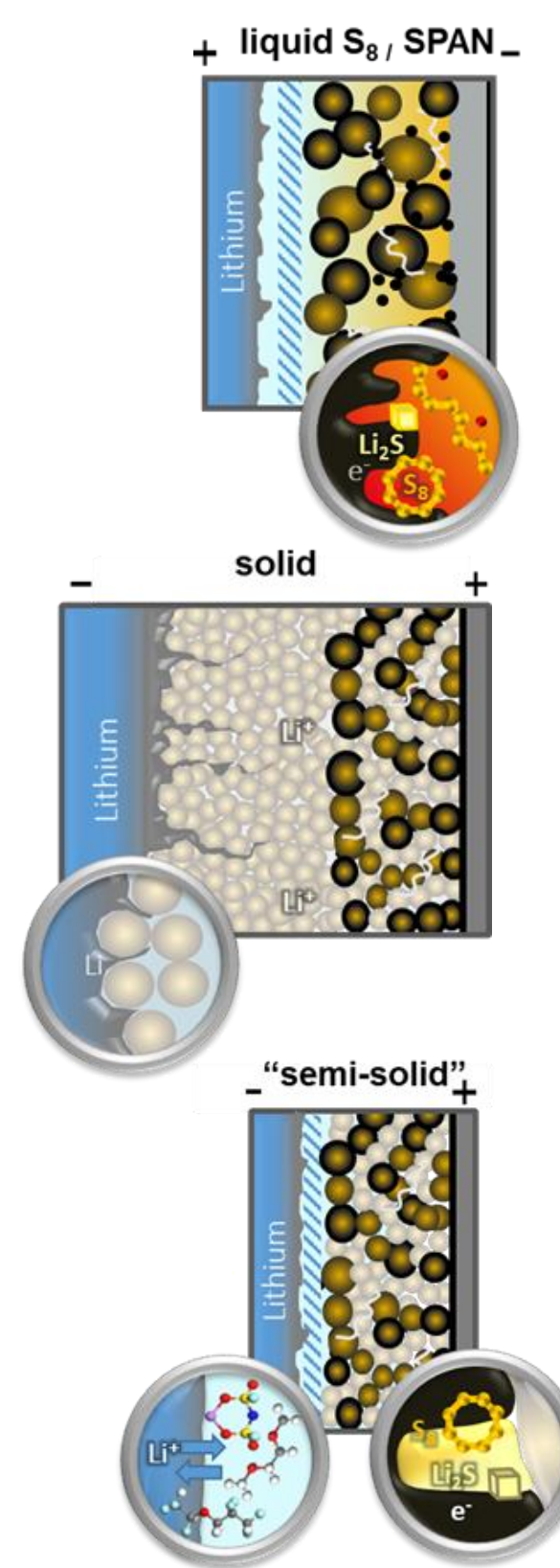
- High theoretical capacity of sulfur (~1672 mAh/g)
- Polysulfide shuttle → lower sulfur utilization

ASSB-Li-S batteries:

- Suppressed PS shuttle → higher sulfur utilization
- Pressure induced Li creeping → short circuits
- High gravimetric energy densities (>500 Wh/kg)

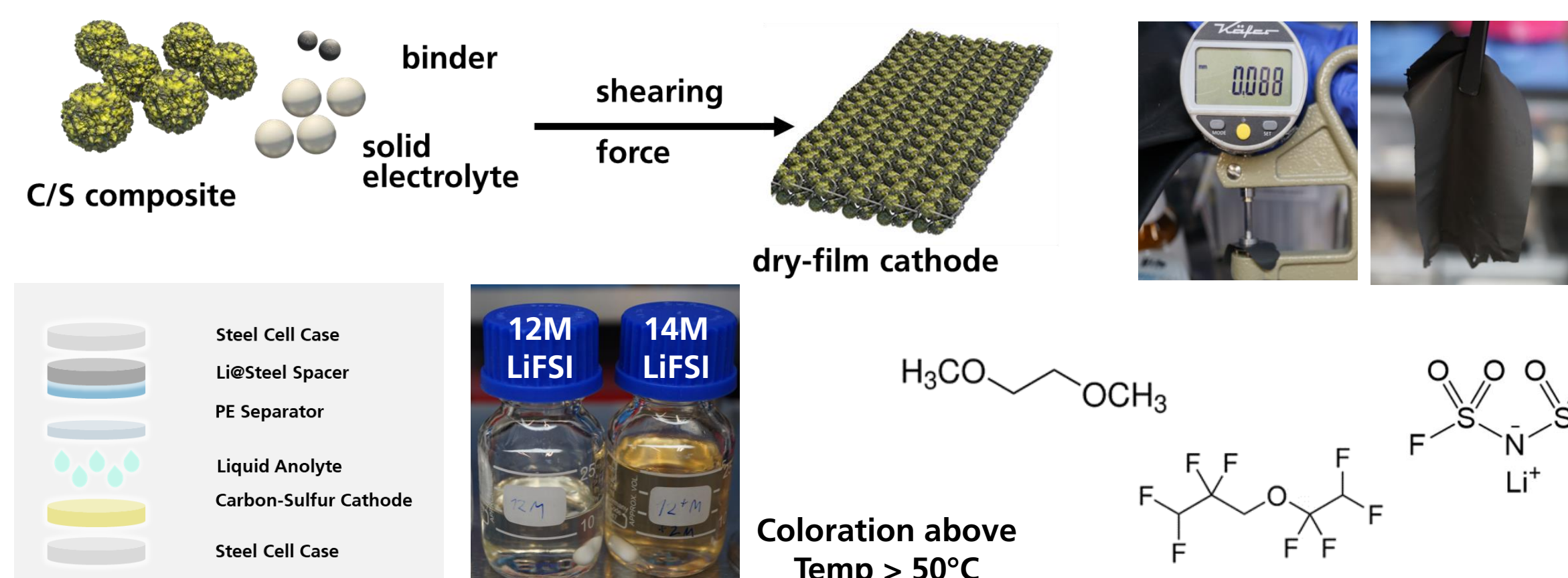
Semi-solid Li-S batteries

- Suppressed PS shuttle by solid conversion and HCE
- Stabilized lithium anode
- High sulfur utilization and longer cycle life



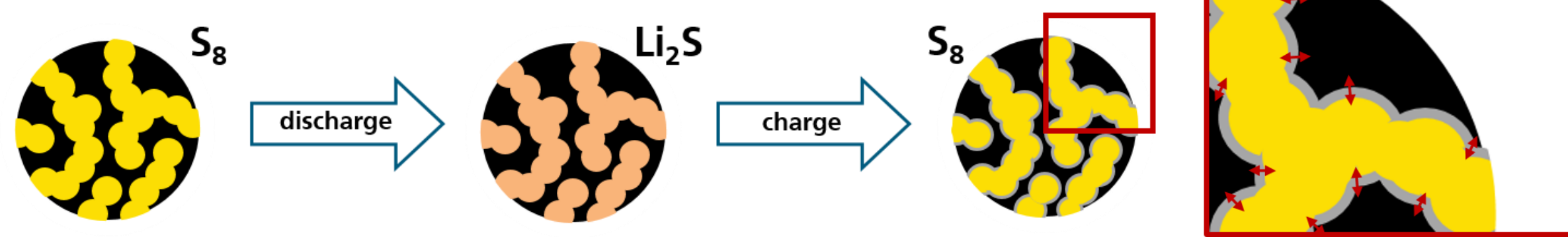
Method

- Solvent-free preparation of dryfilm cathode containing solid catholyte
- Preparation of high-concentrated liquid electrolytes (HCE) and locally high-concentrated electrolytes by dilution with fluoroethers
- Assembly of prototype coin and pouch cells vs. Li metal (no In)



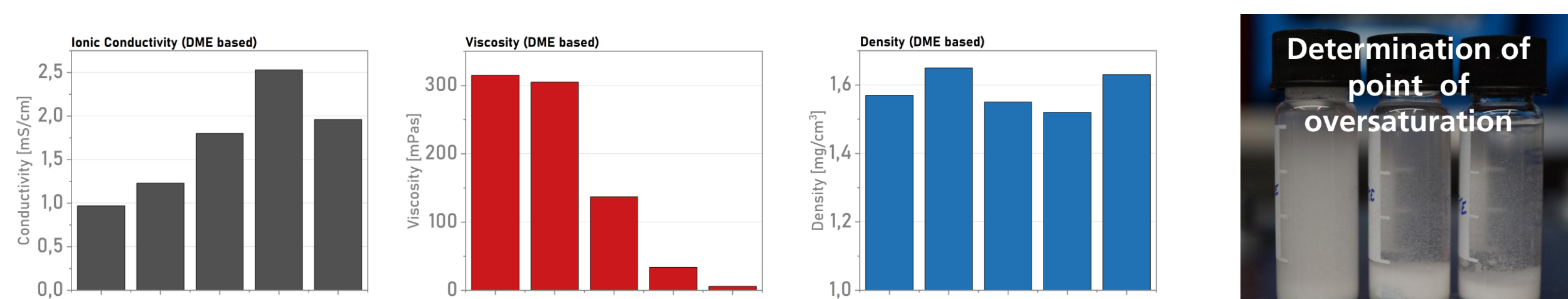
Challenges of dryfilm cathodes

- Sulfur/Li₂S insulating → balancing of ionic & electronic pathways
- Time-consuming, laborious ball-milling needed
- No retention of active material against LE



Challenges of high-concentrated electrolytes

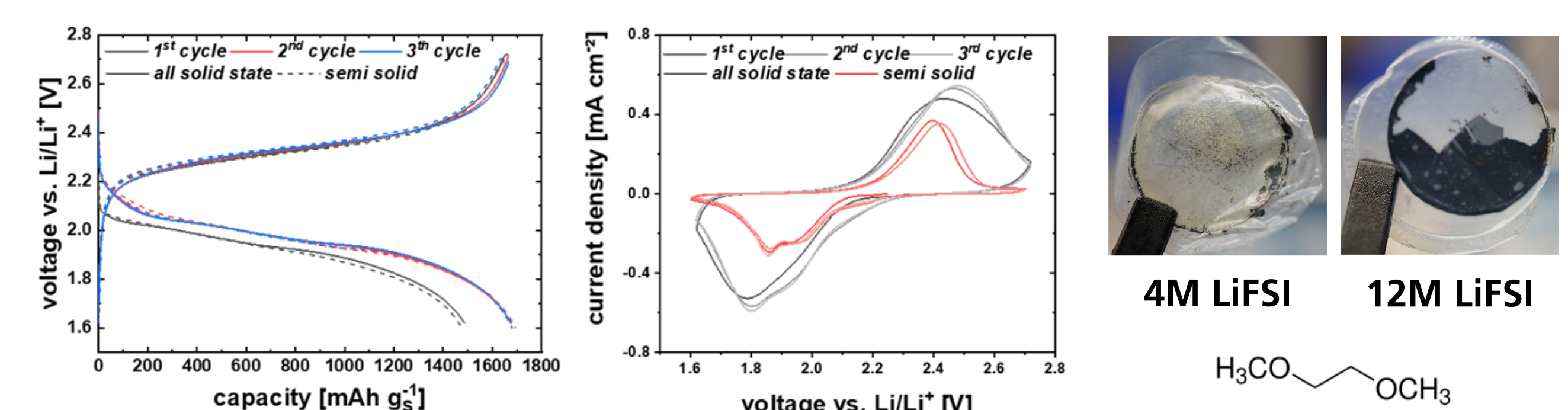
- High viscosity and low mobility → dilution with fluoroethers
- Sidereactions with SE and decomposition at Li anode



Results

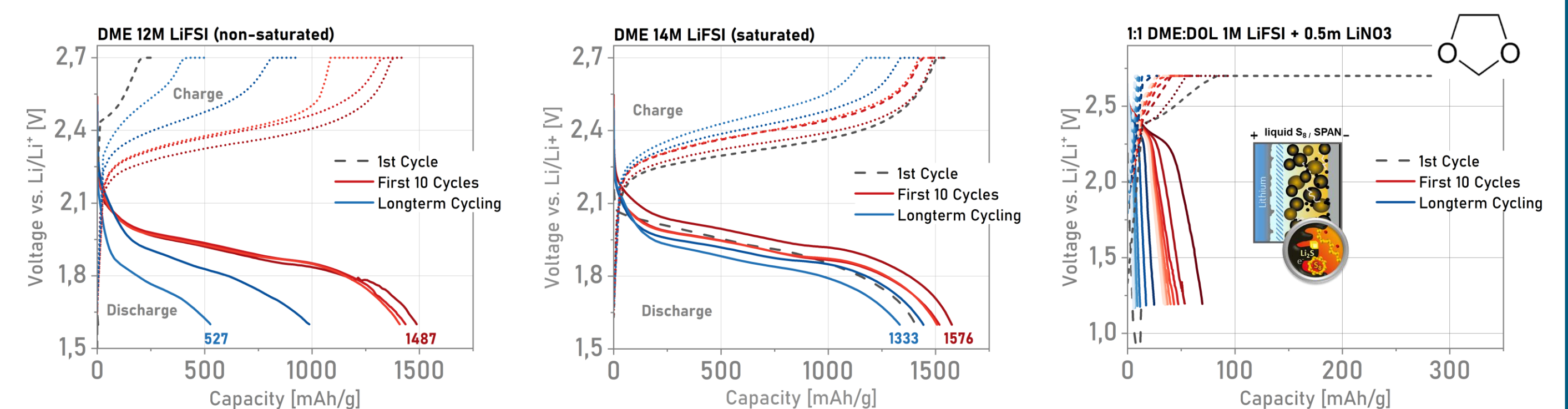
Solid cathode conversion of sulfur to Li₂S

- Dryfilm cathode performs equal in ASSB and semi-solid cells
- Polysulfide formation is intrinsically restrained



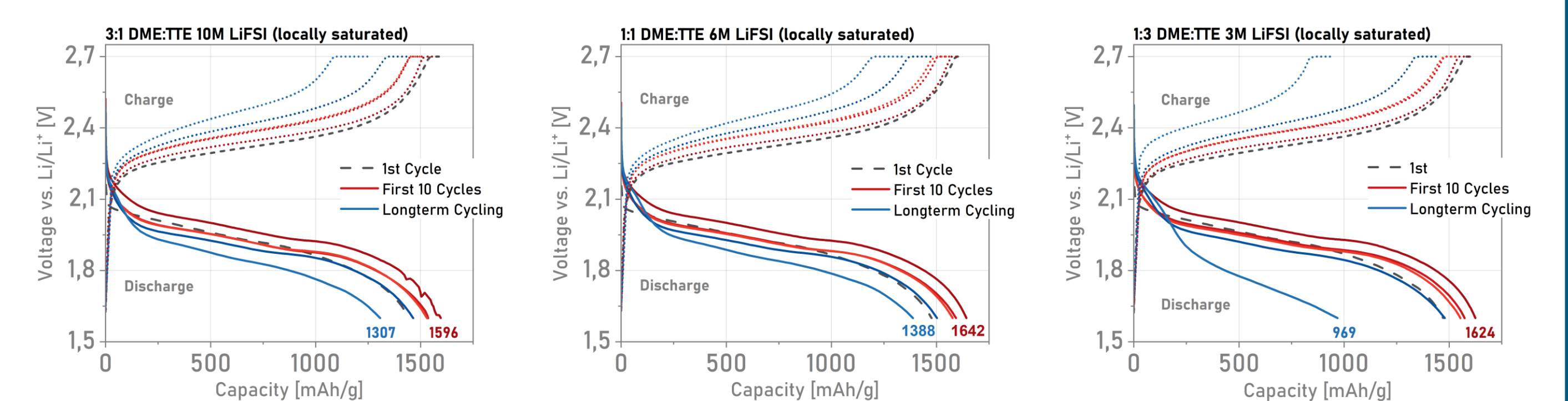
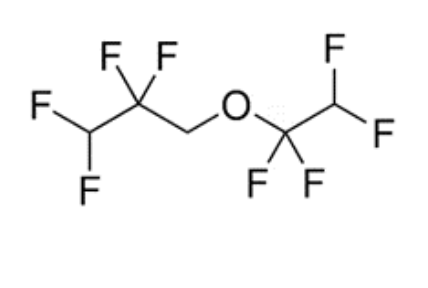
Adjustment of the polysulfide solubility within the LE

- Widely used DME:DOL 1M LiFSI + LiNO₃ electrolyte shows too high sulfur solubility → irreversible reaction with Li₆PS₅Cl
- Non-saturated electrolyte still shows polysulfide (PS) shuttle and capacity loss



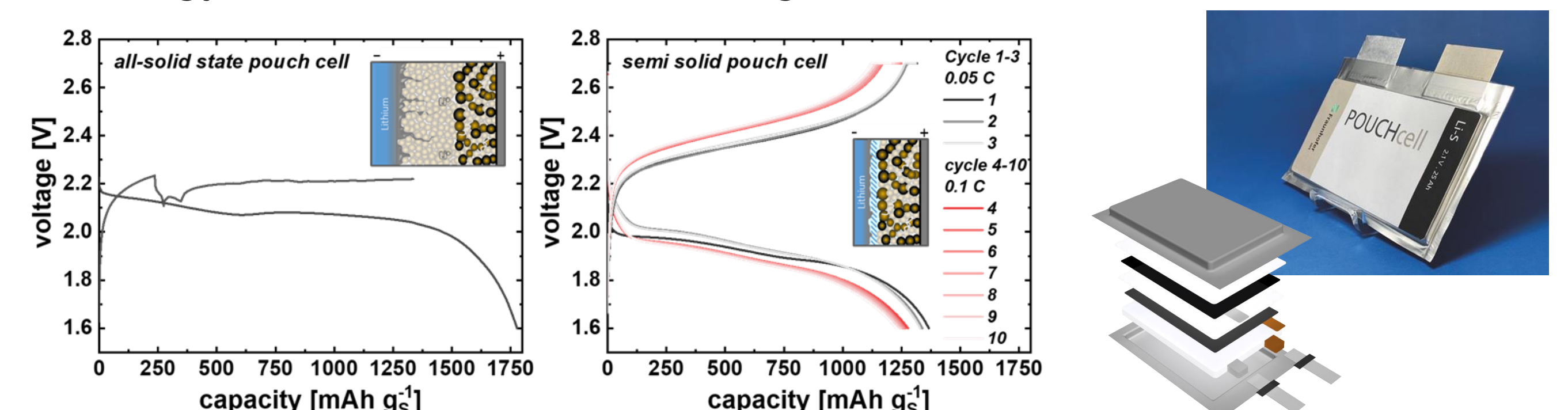
Viscosity adaption by hydrofluoroether addition

- Lower overall salt concentration but still locally saturated
- Viscosity is lowered and ionic conductivity is increased
- But too high TTE content leads to shortened cycle life



Transfer of semi-solid system into pouchcells

- Single-layered ASSB pouchcells without adapted separator membrane fail due to Li dendrites
- Feasible assembly of single-layered pouchcell leading to projected energy densities above 600 Wh/kg



Conclusion

- Proof of concept for semi-solid approach for combination of sulfidic dryfilm cathodes and etherbased high-concentrated electrolytes
- Suppressed PS shuttling and stable interfaces if anolyte is (locally) saturated and fluoroether content is not too high
- Successful transfer into pouchcells with outperforming projected energy densities (>600 Wh/kg)